1938

The development of a zinc phosphate dental cement.

D. O. Myatt
University of Louisville

UNIVERSITY OF LOUISVILLE

THE DEVELOPMENT OF A ZINC PHOSPHATE DENTAL CEMENT

A Thesis

Submitted to the Faculty of

The Graduate School in Partial

Fulfillment of the Requirements

for the Degree of

Master of Chemical Engineering

Department of Chemical Engineering

By

D. O. Myatt

1938

DEVELOPMENT

OF A ZINC PHOSPHATE DENTAL

CEMENT

Director: Dr. L.C. Ernst

Approved by Reading Committee:

.....

.....

.....

.....

May 25, 1938

Acknowledgment

-o-

The author of this thesis gratefully acknowledges the helpful advice and criticism of Dr. R. C. Ernst, director of this research.

-o-

TABLE OF CONTENTS

-o-

Page

Title Page 1

Acknowledgment 3

List of Illustrations 5

List of Tables 6

I. Introduction 7

II. Historical 9

III. Theory 13

IV. Apparatus 21

V. Procedure 29

VI. Data and Results 33

VII. Conclusions 50

Appendix 53

Bibliography 67

-o-

List of Illustrations

-o-

Figure		Page
1.	Gas Furnace in Operation	23
2.	Ball Mill	25
3.	Equipment for Mixing Cement	25
4.	Humidity Apparatus for Setting Time Determination Under Oral Conditions	25
5.	Apparatus for Determining Film Thickness	27
6.	Apparatus for Vacuum Determination of Powder Density	27
7.	Equipment for Determining Cement Consistency	28

-o-

List of Tables.

-o-

Table No.		Page
I.	Comparison of Experimental and Standard Test Results	35
II-a.	Effect of Temperature and Time on True Specific Gravity of Zinc Oxide	37
II-b.	Effect of Temperature and Time on True Specific Gravity of Zinc Oxide-Magnesium Oxide Mixtures	38
III.	Physical Characteristics of Zinc Oxide-Magnesium Oxide Powders (Sample No. 9)	40
IV.	Physical Characteristics of Zinc Oxide-Magnesium Oxide Powders (Sample No. 10)	41
IV-a.	Physical Characteristics of Zinc Oxide-Magnesium Oxide Powders (Sample No. 10, screened)	42
V.	Physical Characteristics of Zinc Oxide-Magnesium Oxide Powders (Sample No. 11)	43
VI.	Physical Characteristics of Zinc Oxide-Magnesium Oxide Powders (Sample No. 12)	44
VII.	Physical Characteristics of Zinc Oxide-Magnesium Oxide Powders (Sample No. 13)	45
VIII.	Effect of Composition Change on Properties of Cement Liquid	48

I. INTRODUCTION.

Zinc phosphate ($ZnHPO_4.3H_2O$) is used as a dental cement and temporary filling material. The cement is formed by the reaction between powdered zinc oxide and liquid phosphoric acid. These materials have been modified so that the product possessed the desired physical and chemical properties for dental use. Manufacturers of dental supplies have surrounded their processes with considerable secrecy. Because of this, very little general knowledge is available regarding the effect of various treatments of the materials upon the characteristics of the product.

The purpose of this investigation was to study the effects of various processing steps on the cement materials and to determine what steps would produce a commercially satisfactory dental cement. Such a cement would conform to the existing standards for zinc phosphate cements. The process should be capable of making the cement in commercial quantities.

-o-

II. HISTORICAL.

The zinc phosphate cements were introduced into dentistry in 1878 by the Rostaing Brothers of Dresden. They used these cements for sealing dental appliances to the oral structure. The cements were also used as a base or foundation for other fillings or for temporary fillings.

The cements used consisted of a powder and a liquid. The powder was a calcined zinc oxide containing boric acid. The liquid was phosphoric acid partially neutralized by zinc phosphate and aluminum phosphate. The materials were mixed just before being applied, as the cement set up rapidly.

The first important article discussing the chemistry of the cements appeared in 1902 (1). It discussed the zinc oxide and phosphoric acid reaction and mentioned the effect of the phosphoric acid neutralizers on the rate of reaction.

Poetschke, (2) in 1916, examined the physical properties of forty dental cements. He reported on the compressive strength and its variation with respect to time. He also investigated the permeability of a few cements and the effect of temperature on the setting time of the cement.

In 1915, Ward and McCormick (3) studied the effect of composition and physical properties on the characteristics of the cement in use in dentistry at that time. They stated that the earlier type of cement, containing alkaline phosphates and borax, was no longer being used. The newer cements were composed of a powder, zinc oxide, mixed with magnesium oxide, and a liquid, phosphoric acid, modified with zinc and aluminum phosphate.

Included in this report was the result of experiments in calcining the zinc oxide and oxidizing the nitrate. Tests were made on these samples to determine their suitability as cement materials. It appeared that the cements used in 1915 were almost identical with the cements in use at the present time.

The National Bureau of Standards (4), in 1933 examined seventeen leading zinc phosphate cements for properties that affected their value as cement materials. Both powder and liquid were analyzed chemically and six physical properties were investigated. The paper did not concern itself with the method of preparation of the materials.

A continuation of this paper appeared in 1934 (5). It completed the investigation with a report on six

other properties. It also contained specifications for a satisfactory cement. (See appendix). These specifications are the standards accepted by investigators in this field, and the techniques which they developed will be used in most cases throughout this investigation.

-o-

III. THEORY.

Zinc phosphate cements are made by mixing a powder, principally zinc oxide, with a liquid, phosphoric acid.

The essential reaction taking place during the mixing and setting of a phosphate dental cement is a reaction between these materials. The reaction may be written:

$$ZnO + H_3PO_4 + 2H_2O = Zn\,HPO_4 \cdot 3H_2O$$

The physical and chemical nature of the reaction and product varies considerably according to the concentration of the acid, the presence of inhibitors or accelerators in either or both liquid and powder, the physical state of subdivision of the powder and the temperature and humidity of the reaction.

The reaction between reagent grade zinc oxide and concentrated phosphoric acid is so rapid under normal conditions that the phosphate is formed upon contact of the two materials. The product possesses little mechanical strength and is crumbly, porous and uneven in composition because of the instantaneous set.

The desired product is hard, relatively tough, impervious to penetration either by water or mouth fluids, insoluble in water or mouth fluids, and sets

slowly enough that a homogeneous mixture may be made and placed in position before setting takes place.

In order to change the characteristics of the reaction and the product, some modification must be made upon either the conditions under which the mixing takes place, the composition of the materials to be reacted, or their physical condition.

The conditions under which the mix may be made are are limited to those ordinarily found in practice, which are around 70°F and 65% relative humidity. It is not advisable, either, to vary the mixing technique (i.e., rate of incorporation of powder and liquid, time of spatulation, etc.), from that recommended for the existing cements because of the commercial disadvantage in trying to sell a cement that must be handled differently from those to which the operator is already accustomed. The only other methods of modifying the product are, therefore, the processing of the materials to alter their physical condition or the addition of varying amounts of other materials to vary composition.

Previous investigations indicate that in the case of the powder the physical condition was the most important, while in the case of the liquid the chemical composition controlled. By this means, an infinite

variation of the properties of the cement may be made. The object of this research was to select those compositions and methods that would result in a satisfactory product.

The character of the cement may be modified by the addition of other materials to the zinc oxide. In this type of cement, magnesium oxide is the only material generally added in excess of one or two percent and it is considered as an accelerator when added, i.e., increases the reaction rate (3).

Small amounts of other compounds have been found in different cements. The Bureau of Standards, investigating sixteen cements, found .1% or more of the following materials present: magnesium oxide, silicon dioxide, bismuth oxide, calcium oxide, copper oxide, barium chromate, barium sulfate, barium oxide, calcium fluoride and boric oxide. Most of these materials were present in such small quantities that one would conclude that they were impurities peculiar to the manufacturing processes or coloring agents added to tint the color to a required shade.

The other important factor affecting the solid was the physical condition of the powder. The rate of a given reaction depends on the physical state of subdivision of the materials. A very fine material would

have a large surface area per unit weight and the chemical reaction would naturally proceed with rapidity. If the zinc oxide particles could be treated so that they would have less surface exposed per unit weight, the rate of reaction would be slower.

Uniformity of size of the particles was also important because of the nature of the powder-liquid reaction. If the powder consists of a large number of small particles and also, some particles considerably larger in size, the reaction rate would vary widely over the reaction period because the surface area of the zinc oxide would vary drastically over that time. A powder that consists of particles with small variations in size has an even rate because there would be no great change in powder surfact at the beginning of the reaction.

The cement liquid may be modified only by a change in chemical composition. The materials that are usually added to the phosphoric acid are aluminum hydroxide, zinc oxide or hydroxide and magnesium oxide or hydroxide (5). Their addition increases the specific gravity and viscosity of the liquid and reduces its reaction rate.

The variation of the properties of the powder and liquid strongly affects the characteristics of the cement reaction. The setting of an actual dental cement pre-

sumably takes place as follows: when the powder and liquid are first mixed, the phosphoric acid dissolves the zinc oxide, gradually building up the concentration of zinc ions in solution. Before the zinc oxide has been completely dissolved, the concentration of zinc ions becomes so great that the zinc phosphate formed begins to precipitate. The mix becomes stiff and gradually hardens to a solid mass as the remaining liquid and powder react slowly to form zinc phosphate.

If the powder is composed of particles that are too small, the particles will all dissolve so rapidly that the cement will begin to set before a thorough spatulation has made the mix homogeneous. On the other hand, particles that are too large will produce a slow-setting cement that will have a tendency to set before the acid has had time to react completely with the zinc oxide. The film thickness of such a cement would be large because of the undissolved particles remaining in the set cement.

A large size-range of the powder particles is undesirable. When a powder of this type is reacted, the initial rate of reaction would be great, as the small particles would contain a relatively large surface area compared to their weight. These small particles would soon be all dissolved and the zinc

phosphate would be precipitating while the larger particles of zinc oxide were still being attacked by the acid. Since the cement will set before the reaction has proceeded stoichiometrically, the set cement prepared in such a manner would consist of relatively large particles of zinc oxide imbedded in a matrix of precipitated zinc phosphate with an excess of phosphoric acid a possible constituent (according to the amount of phosphoric acid used to make the mix). The presence of unreacted phosphoric acid in the set cement is quite undesirable as it will leach out and leave the cement porous. The method of mixing counteracts to some extent the effect of variations in particle size on the reaction but cannot completely eliminate the difference, particularly where a large size-range is encountered.

The chemicals that are in the cement liquid also affect the reaction. The addition of aluminum hydroxide will lower the rate of reaction and increase the viscosity of the mix. If zinc hydroxide is added, the rate of the reaction will be decreased, but the presence of the zinc ions in the liquid will cause zinc phosphate to precipitate earlier in the reaction than it would if the acid had been neutralized to the same extent by aluminum

hydroxide. The presence of magnesium ions in a liquid that is mixed with a powder containing magnesium oxide will similarly affect the precipitation of magnesium phosphate. Dilution of the liquid with water is necessary as the set cement contains water of hydration. Too much water in the cement liquid, however, will produce a porous cement as the excess water will be trapped in it.

A desirable cement would have the following characteristics. The liquid and powder when mixed to the proper consistency should be in stoichiometric proportions. The powder should be composed of small particles, all near the same size. The liquid should have only enough water in it to satisfy the chemical reaction. The mixed and set cement should conform to the specification for zinc phosphate cement (4).

-o-

IV. APPARATUS.

The principle pieces of apparatus used were a gas fired furnace and a ball mill. The furnace was an injector gas furnace. (See Fig. I). The inside dimensions were six inches diameter by six and one-half inches height, which permitted the use of a magnesia crucible that was five and one-half inches in height and two and three-quarters inches outside diameter with a capacity of three hundred grams of charge, which was a satisfactory amount for the experimental runs being made. The design of the furnace permitted the use of the city gas available and the laboratory compressed air.

The temperature attainable by the furnace was affected by the B.T.U. content of the gas and the humidity of the air, but under favorable conditions it could reach 1500 C.

The ball mill was a porcelain ball mill of one quart capacity, charged with silica balls. (See Fig. 2).

These two pieces of equipment provided the two main methods by which the cement powder was processed. The only other piece of equipment used for that purpose was a screen. It was a bolting cloth screen with a mesh opening of 20 microns.

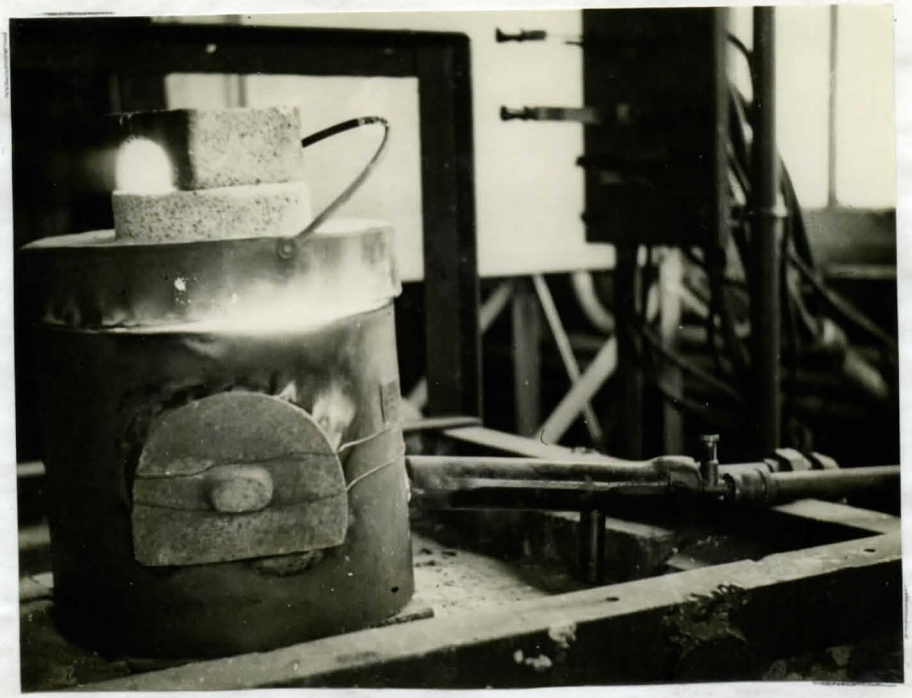

Fig.1 Gas Furnace in Operation

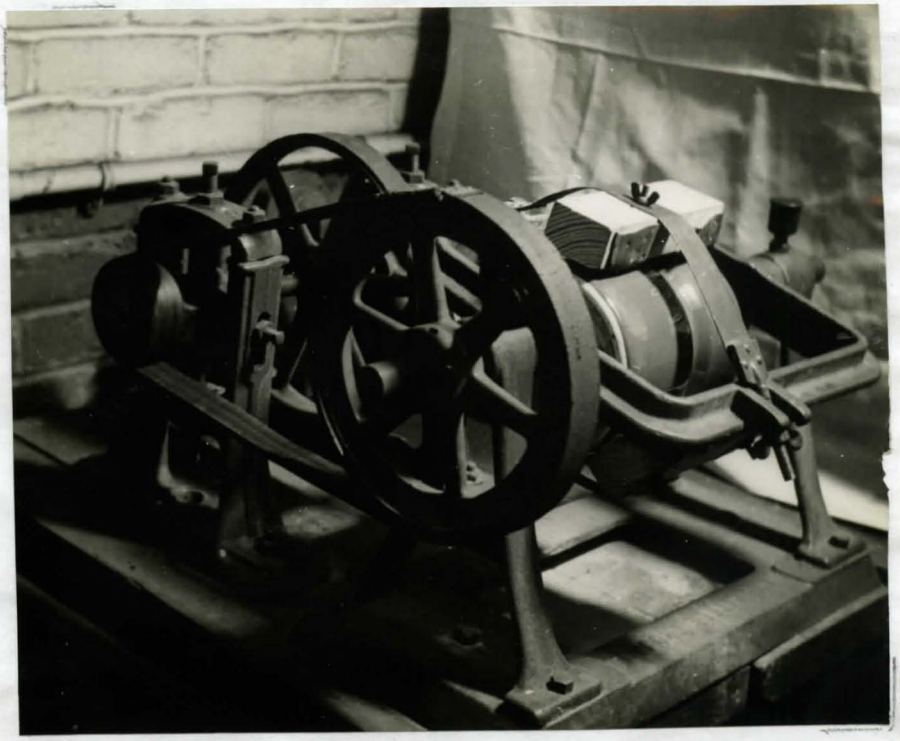

Fig. 2 Ball Mill

Several pieces of apparatus were used in testing the cement. The special equipment was patterned as exactly as possible after the description of the equipment used for the same testing purposes at the Bureau of Standards. A description of each piece of apparatus follows:

I.- Equipment for Mixing the Cement.

This equipment consisted of a dentist's mixing slab with an embedded thermometer, a spatula, a hypodermic syringe, capacity 1 cc and graduated in hundredths, and a stop-watch, graduated in fifths of a second. (See Fig. 3).

2.- Equipment for Determination of Setting Time.

This equipment consisted of a humidifying chamber containing a thermometer. (See Fig. 4). It was constructed from a dessicator, with a waterproof cardboard top that had a flap cut in it. A platform inside supported a glass plate which held the cement being tested. A Gilmore needle weighing one pound and having a flat end one-twenty-fourth of an inch in diameter was used in testing the cement. A small glass ring held the cement. The temperature was controlled by pouring hot water into the bottom of the jar. This equipment was used for the determination of setting time under oral conditions, namely,

Fig. 3 Equipment for Mixing Cement

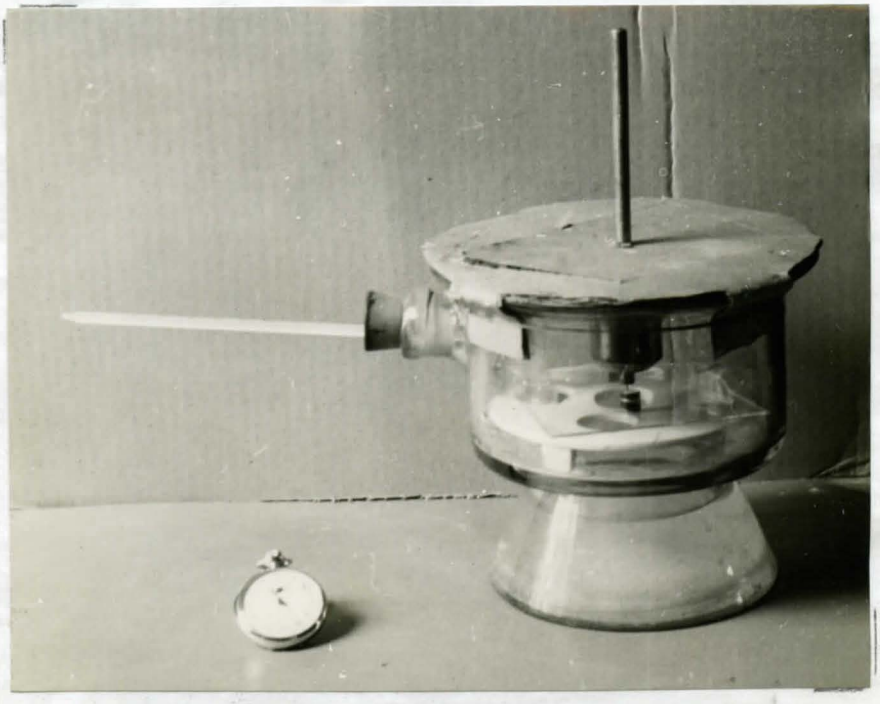

Fig. 4 Humidity Apparatus For Setting Time Determination Under Oral Conditions.

99° F and saturation.

3.- Equipment for Determining Film Thickness.

Two glass plates, cut and ground to a dimension of 1 cm x 2 cm, a bottom block in which they were supported and an apparatus for imposing a weight of fifteen kilograms on the plates were used to determine the film thickness of the cement. (See Fig. 5). To measure the film thickness after the plates had been pressed, a thickness gage was used which measured thicknesses in thousandths of an inch and permitted estimation to two ten-thousandths.

4.- Equipment for Determining Particle Size.

A microscope equipped with a condensor for the adjustment of sub-stage lighting and having as lens equipment a 4 mm objective and a 7.5 X ocular with an ocular micrometer provided the means for determining the powder particle size.

5.- Equipment for Determining Density.

This consisted of a Geissler pycnometer with thermometer and a bell jar. (See Fig. 6).

6.- Equipment for Determining Consistency of Fresh-Mixed Cement.

A hollow glass tube, fitted with a glass plunger and a rubber plug, graduated to deliver 1/2 cc of material, and two glass plates with a weight

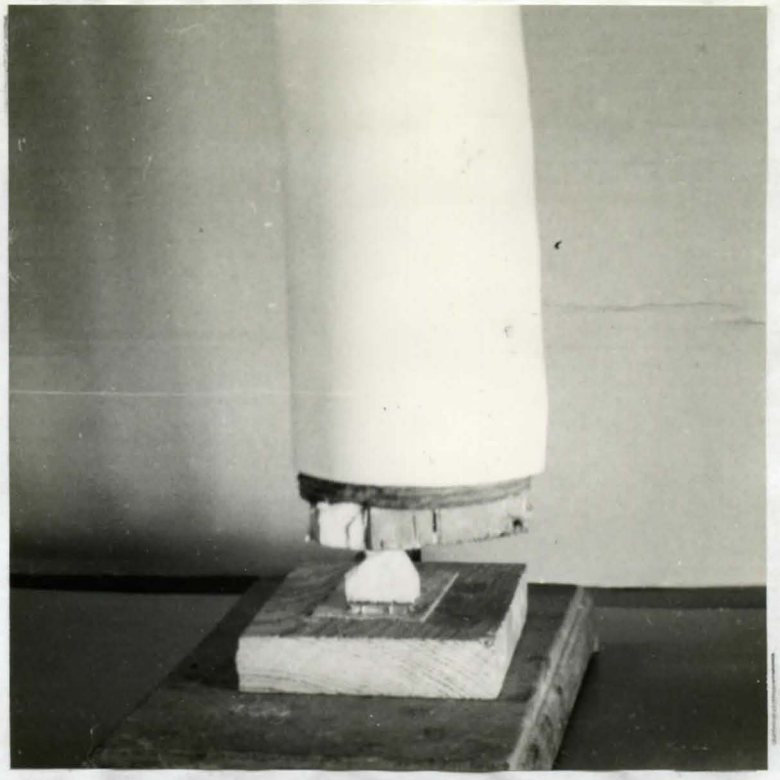

Fig. 5 Apparatus for Determining Film Thickness

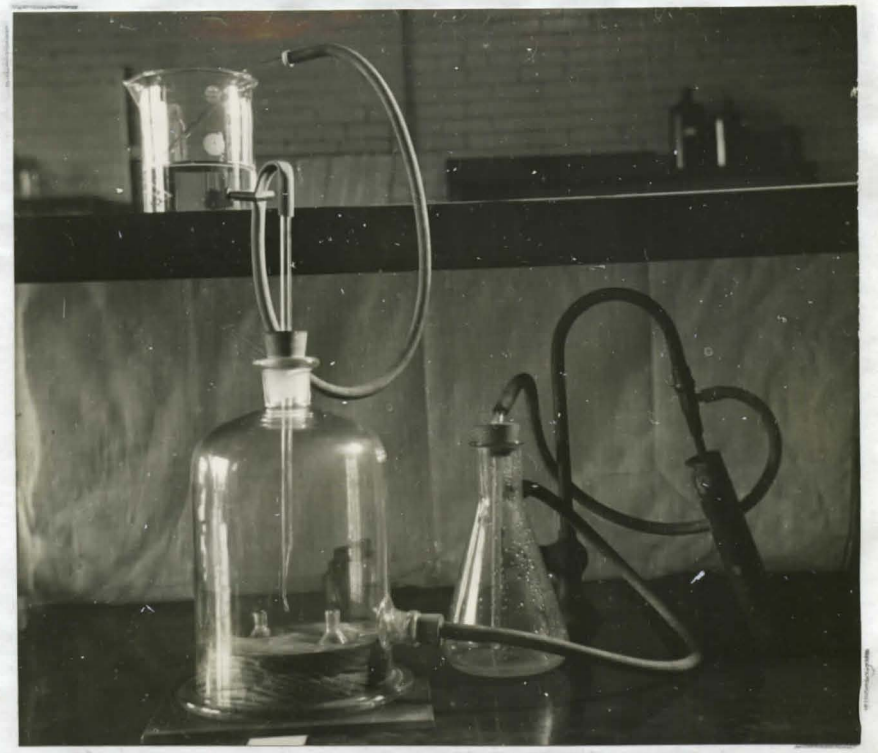

Fig. 6 Apparatus for Vacuum Determination of Powder Density

to make the total weight of the top plate and the weight 120 grams, made possible the measurement of the cement consistency. (See Fig. 7).

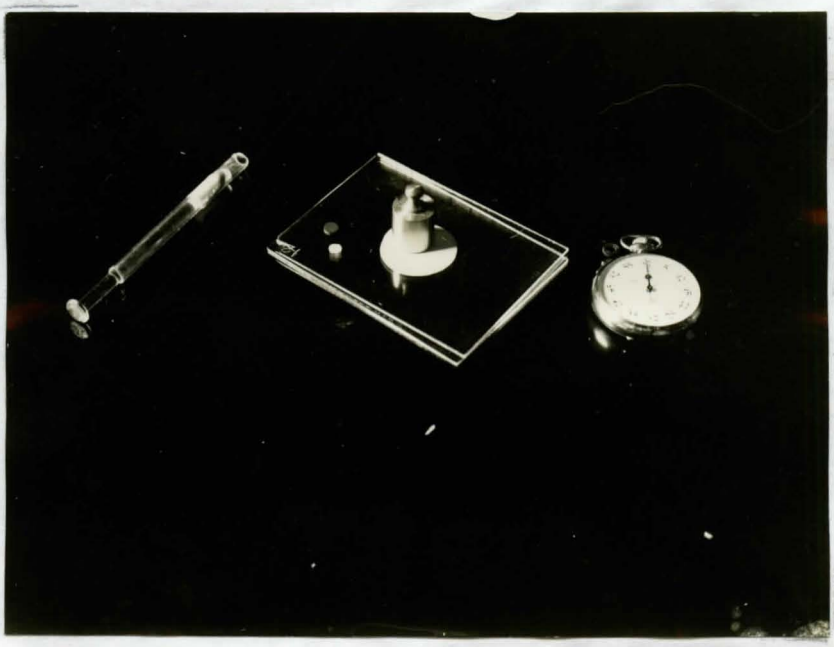

Fig.7 Equipment for Determining Cement Consistency

V. PROCEDURE.

The characteristics of the cement were determined by the use of the following tests adopted by the Bureau of Standards. (4)(5).

A. For the Powder:

1. Chemical Composition
2. Specific Gravity
3. Particle Size and Size Distribution

B. For the Liquid:

1. Chemical Composition
2. Specific Gravity

C. For the Mixed Cement:

1. Setting Time

   a. Under Room Conditions (65% Humidity, 70 F).
   b. Under Oral Conditions (100% Relative Humidity, 99 F).

2. Consistency of Unset Cement
3. Film Thickness of Cement

The determination of the above properties was expected to show whether the material tested was suitable as a cement. A technique of analysis was developed that would produce results checking the method of previous investigators. The results obtained by the author were checked by comparing his analyses with those reported by the Bureau of Standards.

A description of the technique of the tests may be found in the appendix.

The materials being studied, zinc oxide and magnesium oxide, were subjected to various processes that affected the property of the material when considered as a cement. The processes were:

1. Change of Chemical Composition
2. Heating
   A. Varying the Temperature
   B. Varying the Time of Heating
3. Grinding Various Lengths of Time
4. Size Separation of Fines or Oversize Particles.

The liquid was subjected only to change of composition. The powder was subjected to all four processes. The effects of the various treatments was then tested and from the results, the best method of preparing the powder was selected.

The manner in which the various processing steps were carried out is explained in the following paragraphs:

1. Change of Chemical Composition.

This was done when the samples were made. The powder mixtures studied most consisted of pure zinc oxide and a mixture of approximately 90 percent zinc oxide and 10 percent magnesium oxide. One mix was tested that contained, in addition to the zinc oxide and magnesium oxide, .3 percent silica added as sodium silicate.

Various proportions of phosphoric acid, water, aluminum hydroxide and zinc hydroxide were tested in developing the liquid.

2. Heating.

Most of the heating of the powder samples was done with the gas fired furnace described in the section "Apparatus." The charge was 300 gm. In the processing, the powder was heated to temperatures between 1100°C and 1500°C for lengths of time varying from one and one-half to nine hours. One run was also made in an electric resistance muffle. The temperature was raised to 1100°C and the duration of the run was two and one-half hours.

3. Grinding Various Lengths of Time.

The cement powders were ground in the ball mill described in the section, "Apparatus". During the grinding, adequate samples of the powder being ground were removed periodically (at approximate two hour intervals) and tests were made on the effects of particle size change on the cement properties.

4. Size Separation of Fines or Oversize Particles.

The particles were passed through a bolting cloth screen having a mesh opening of twenty microns (.02mm).

DATA AND RESULTS

The experimental results obtained are listed in Tables I to VIII. The comparison of the author's testing results with those obtained by the Bureau of Standards is shown in Table I. The effect of temperature and time on the true specific gravity of various powder materials is shown in Tables II-a and II-b. The physical characteristics of the powders prepared are listed in Tables III to VII. Table VIII shows how the composition of the liquid affects the setting time of the cement and the specific gravity of the liquid.

-o-

TABLE I.

Comparison of Experimental and Standard Test Results.

-o-

Test (All tests made on Fleck's "Snow-White" Cement)	Result by Bureau of Standards	Experimental Result
True Specific Gravity of Cement Powder	5.16 ± .02	5.13 5.13
Specific Gravity of Cement Liquid	1.56	1.561 1.561 1.561
Setting Time of Cement, Room Conditions	16 min.	16 min.30 sec. 15 min.
Setting Time of Cement, Oral Conditions	7 min.	7 min. 7 min.15 sec.
Film Thickness of Cement	17 microns	20 microns 20 microns 18 microns 18 microns
Consistency of Freshly Mixed Cement (Diameter of Disc)	34 mm	36 mm 36 mm 36 mm

The agreement of the author's testing results with those of the Bureau of Standards enabled the findings of this research to be correlated with those of the Bureau of Standards. All of the determinations agreed within the limit of experimental error. The gage used in the film thickness determinations was graduated in thousandths of an inch, permitting estimation to two ten-thousandths, or about four microns. This determination, therefore, was not as accurate as was desired, but was satisfactory in indicating the relative film thickness.

-o-

TABLE II.-a.

Effect of Time and Temperature on

Specific Gravity of Zinc Oxide.

-o-

No.	Sample	Treatment	True Sp. Gr.		Avg.
1	ZnO, Mallinckrodt Analytical Reagent	None	5.57	5.50	5.54
2	ZnO, Kahlbaum Heavy Impalpable For Dentists	None	5.52	5.60	5.56
3	ZnO, Kahlbaum Heavy Crystalline For Dentists	None	5.56	5.59	5.57
4	ZnO, Mallinckrodt Analytical Reagent	3½ hr. to 1150°C	5.62	5.67	5.65
5	ZnO, Mallinckrodt Analytical Reagent	6 hr. to 1200°C	5.60	5.63	5.62
6	ZnO, Mallinckrodt Analytical Reagent	1½ hr. to 1000°C	5.60	5.63	5.62
7	ZnO, Mallinckrodt Analytical Reagent	9 hr. to 915°C	5.56		5.56
8	$Zn(NO_3)_2 6H_2O$, Mallinckrodt. Analytical Reagent	Ignited to the Oxide, Heated to Dull Red	5.57		5.57

TABLE II.- b.

Effect of Time and Temperature on

Specific Gravity of

Zinc Oxide Magnesium Oxide Mixtures

-o-

No.	Composition	Time of Heating, Hours	Temp. of Heating, Degrees C	% Loss on Heating	True Sp. Gr.
9.	90% ZnO 10% MgO	5¾	1280	22	5.07
10.	90% ZnO 10% MgO	1¾	1316	15	5.11
11.	90% ZnO 10% MgO	3¼	1350	10	5.10
12.	89% ZnO 9% MgO 2% H_3BO_3	2	1244	13	4.92
13.	89.7% ZnO 10.0% MgO 0.3% SiO_2	2½	1090	5	4.77

Tables II-a and II-b disclose the fact that the method of treatment of powders of any certain composition had very little effect on their true specific gravity. The addition of small amounts of other materials, however, changed the specific gravity considerably.

The material lost by volatilization increased as the time of heating and the temperature increased. The effect began at temperatures around 1200°C.

TABLE III

Physical Characteristics of ZnO and MgO Powders

(Sample 9)

-o-

Time Ground, Hours	2½	4	5½	7	10½
Max. Particle Size, Microns	40	32	24	24	12
Min. Particle Size, Microns	2	2	1	1	1
* Setting Time, Room Conditions, Minutes	50	33	25	20	14
*Setting Time, Oral Conditions, Minutes	12	10	8½	7	6
* Film Thickness, Microns	48	48	43	41	59
* Consistency (Diam. Disc, mm)	41	42	36	34	31

* The liquid used in the mixed cement had the following composition:

PO_4 57.9%, Al 2.8%, Mg 0.3%. H_2O 39.0%

TABLE IV

Physical Characteristics of ZnO and MgO Powders

(Sample 10)

-o-

Time Ground, Hours	2½	4½	6½	8½	10½	13½
Max. Particle Size, Microns	35	30	30	30	25	20
Min. Particle Size, Microns	2	2	2	2	2	2
* Setting Time, Room Conditions, Minutes	34	27	23	21½	17	13
* Setting Time, Oral Conditions, Minutes	11½	8½	6½	5½	5	4½
* Film Thickness, Microns	48	22	20	27	20	36
* Consistency (Diam. Disc, mm)	36	38	35	34	32	27

* The liquid used in the mixed cement had the following composition:

PO_4 57.9%, Al 2.8%, Mg 0.3%, H_2O 39.0%

TABLE IV - a

Physical Characteristics of ZnO and MgO Powders

(Sample 10, Passed Through Screen, 20 Micron Mesh Opening)

-o-

Time Ground,	2½	4½	6½	8½	10½	13½
Max. Particle Size, Microns	20	20	20	20	20	20
Min. Particle Size, Microns	2	2	2	2	2	2
* Setting Time, Room Conditions, Minutes	24	21	17	15	15	16
* Setting Time, Oral Conditions, Minutes	8½	9	6½	6	6	5½
* Film Thickness, Microns	38	28	23	32	46	56

* The liquid used in the mixed cement had the following composition:

PO_4 57.9%, Al 2.8%, Mg 0.3%, H_2O 39.0%

TABLE V

Physical Characteristics of ZnO and MgO Powders

(Sample 11)

-o-

Time Ground, Hours	1½	3½	5½	7½	9½	12½
Max. Particle Size, Microns	60	40	36	40	24	16
Min. Particle Size, Microns	4	2	2	2	1	1
* Setting Time, Room Conditions, Minutes	More Than 50	More Than 50	43	35	30	25
* Setting Time, Oral Conditions, Minutes	15	13½	9½	12	10½	8½
* Film Thickness, Microns	74	64	53	43	41	33
* Consistency, (Diam. Disc, mm)	44	49	50	46	43	38

* The liquid used in the mixed cement had the following composition:

PO_4 57.9%, Al 2.8%, Mg 0.3%, H_2O 39.0%

TABLE VI

Physical Characteristics of ZnO and MgO Powders

(Sample 12)

-o-

Time Ground, Hours	2½	5	7½	9	11
Max. Particle Size, Microns	45	35	35	28	24
Min. Particle Size, Microns	2	2	2	1	1
* Setting Time, Room Conditions, Minutes	40	32	23	21½	15
* Setting Time, Oral Conditions, Minutes	11	12	11	10	8
* Film Thickness, Microns	46	48	51	46	58
* Consistency (Diam. Disc, mm)	41	41	40	37	35

* The liquid used in the mixed cement had the following composition:

PO_4 57.9%, Al 2.8%, Mg 0.3%, H_2O 39.0%

TABLE VII

Physical Characteristics of ZnO and MgO Powders

(Sample 13)

-o-

Time Ground, Hours	2	4½	6½	8½	10½	13½
Max. Particle Size, Microns	1	1	-	-	-	-
Min. Particle Size, Microns	1	1	-	-	-	-
* Setting Time, Room Conditions, Minutes	8	6	-	-	-	-
* Setting Time, Oral Conditions, Minutes	4	5	-	-	-	-
* Consistency (Diam. Disc, mm)	26	21	-	-	-	-

* The liquid used in the mixed cement had the following composition:

PO_4 57.9%, Al 2.8%, Mg 0.3%, H_2O 39.0%

This series of runs revealed that a temperature of more than 1100 C was necessary to produce a material with satisfactory reaction characteristics. Grinding the cement in the ball mill decreased the particle size of the powder, the setting time under both room conditions and oral conditions and increased the consistency of the fresh-mixed cement. The film thickness was at first decreased, to be followed in some cases (Tables III, IV, IV-a and VI) by an increase as the powder grew finer. This occurred because the film thickness was controlled by two variables: particle size and cement consistency. The samples that showed an increased film thickness for the finest ground powders produced stiff cement mixes.

The length of time the powders needed to be ground to reduce them to a given particle size depended greatly upon the temperature and time of heating. The powders that had been subjected to high temperatures had a larger particle size than those fired at a lower temperature and ground the same length of time.

Most of the charges reduced to a smooth powder after several hours grinding and reached a particle size satisfactory for dental use in from six to nine hours.

Screening to eliminate oversize particles increased the reaction rate of the cement and produced a final material that was superior to the unscreened powder. The film thickness was less and the rate of reaction was more uniform.

-o-

TABLE VIII

Effect of Composition Change on Properties of Cement Liquid

-o-

Composition					Results		
H_3PO_4 (90%) Grams	$Zn(OH)_2$	$Al(OH)_3$	$Mg(OH)_2$	H_2O	* Setting Time, Minutes Room	Oral	Specific Gravity
66.4	0	4.29	.515	28.8	15	6	1.50
66.4	0	8.1	.725	24.8	18	7	1.54
66.4	0	10.0	0	23.6	11½	5½	1.58
66.4	0	0	5.0	28.6	3½	3½	1.49
66.4	5.0	0	0	28.6	3	2½	1.46
66.4	0	0	0	33.6	2	2	1.41

* All Liquids Were Mixed with Fleck's "Snow White" Powder

Addition of aluminum hydroxide, zinc hydroxide or magnesium hydroxide in the cement liquid decreased the reaction rate of the cement mixture and lessened the thermal effect of the reaction. The cement made with the acid that had not been neutralized set almost immediately and the heat of reaction made the cement almost too hot to touch.

Very little difference in setting time under room and oral conditions appeared to characterize the addition of magnesium hydroxide. The addition of aluminum hydroxide produced a cement that exhibited a two-fold difference in setting time between room and oral conditions.

The specific gravity and viscosity of the liquid were both increased by the addition of the various materials.

-o-

VII. CONCLUSIONS.

The investigation consisted of the development of a zinc phosphate dental cement.

The cement powder was prepared by subjecting zinc oxide and mixtures of zinc and magnesium oxides to temperatures ranging between 1100 C and 1500 C, and to grinding that reduced the maximum particle size of the product to as small as fifteen microns.

The cement liquid used was prepared by combining in suitable proportions phosphoric acid, aluminum hydroxide, magnesium hydroxide and water.

The powder found to be most satisfactory was a mixture of 90 percent zinc oxide and 10 percent magnesium oxide fired approximately 2 hours to a temperature near 1325 C and ground in a ball mill 6 hours.

The most suitable liquid was a mixture of phorphoric acid, aluminum hydroxide, magnesium hydroxide and water, combined in the following proportions:

H_3PO_4 (90% By Wt)	66.4 gm
$Al(OH)_3$	8.1 gm
$Mg(OH)_2$	.725 gm
H_2O	24.8 gm

The properties of the powder that were studied were particle size, specific gravity, and composition.

The properties of the liquid that were studied were specific gravity and composition. The cement was investigated for consistency, setting time under room and oral conditions, and film thickness.

Further and more exhaustive tests would be necessary to report in detail the effect of the treatment on every property of the cement. Such a project is beyond the scope of this investigation.

-o-

APPENDIX

American Dental Association
Tentative Specification No. 8 for
Dental Cementing Medium.

(Effective July 1, 1935)

"A. General Specification: This specification is for dental cements, the primary uses of which are:

A-1. To join or to seal dental appliances to oral structures or to other appliances.

A-2. To serve as a base or foundation for other filling material.

A-3. To serve as a temporary filling material.

B. Types. Only one type of material is specified. The consistency of the mix which different uses require can be varied by the individual operator to suit his own needs.

C. Material: C-1. These cements shall consist of a powder and a liquid which, when mixed in the proper manner, will harden or set.

C-2. The powder and liquid shall be uniform and free from poisonous foreigh materials.

C-3. Colors for the set cement shall be specified by the purchaser.

D. General Requirements: D-1. The liquid shall be free from cloudiness, precipitation, deposits or sediment.

D-2. Cements when spatulated in the proper dental manner shall not:

D-2a. Form lumps or granules.
D-2b. Evolve gas.
D-2c. Contain known pulp devitalizing agents such as arsenic.
D-2d. Discolor tooth structures.

E. Detail Requirements: E-1. Time of setting. The time of setting shall not be less than four nor more than ten minutes.

E-2. Ultimate Compressive Strength. The ultimate compressive strength shall not be less than:
E-2a. 350 kg. per square centimeter (approximately 5000 pounds per square inch) for specimens crushed one hour after mixing.
E-2b. 840 kg. per square centimeter (approximately 12,000 pounds per square inch) for specimens crushed seven days after mixing.
E-3. Film Thickness (see paragraph 1). The film thickness shall not exceed 0.05 mm (0.002 in.).
E-4. Disintegration (see paragraph J). The disintegration of the cement shall not exceed 1.0 percent by weight after immersion for seven days in distilled water.

F. Methods of Inspection and Test: F-1. Preparation of the Test Specimens. The preparation of the test specimens shall be conducted at a temperature between 65 and 75 F. and at a relative humidity between 55 and 75 percent. The powder: liquid ratio used shall be determined by the consistency test. The mixing technics employed in the preparation of all test specimens shall be those which accompany the packages of cement except that the temperature and humidity may vary within the foregoing limits. All apparatus and instruments shall be clean, dry and free from particles of hardened cement.

F-2. Testing Consistency. One type of apparatus for measuring consistency is shown in Figure 1. This apparatus consists of a glass tube (inside diameter approximately 6.5 mm) which will deliver a definite volume (0.5 cc) of mixed cement, two flat plates and a weight. (The combined weight of the top plate and the weight shall be 120 gm).

F-2a. Trial amounts of powder are mixed with 0.5 cc of liquid. Then 0.5 cc of mixed but unset cement is placed in a measuring device and deposited on a flat glass plate. Three minutes after the mix is started, another glass plate (weighing approximately 20 gm) and the additional weight shall be carefully placed on the soft cement. Trials shall be made until the average of the major and minor diameters of the slumped mass of cement shall be 30 - 1 mm ten minutes after starting the mix. The average of the amounts of powder used in three such determinations shall be the amount of powder (combined with 0.5 cc of liquid) necessary to produce a mix of standard consistency.

F-3. The tests for arsenic and similar poisonous materials shall conform to those designated by the United States Pharmacopeia (current edition).

G. Time of Setting. A ring 5 mm high and 10 mm in diameter is placed on a flat plate and filled with cement of standard consistency. Three minutes after the mix is started, the specimen is transferred to an atmosphere of 100 percent relative humidity of 99°F. A standard Gillmore needle (weighing 1 pound and having an end one-twenty-fourth inch in diameter) is lowered vertically until the surface of the cement is touched. This is repeated at frequent intervals. The time of setting shall be the number of minutes elapsed from the starting of the mix to the time when the needle fails to make a perceptible circle on the surface of the specimen. The setting time shall be reported to the nearest minute.

H. Ultimate Compressive Strength: A cylindrical mold 12 mm high and 6 mm in diameter is placed on a flat plate and slightly overfilled with cement of standard consistency. A second flat plate is pressed on top of the mold to remove excess cement. The molds shall be made of hard rubber, glass or other substance that will not be corroded by the cement. (Painting the molds with a thin solution of a hard wax in benzene will facilitate removal of the specimens). Three minutes after the mix is started, the molds are transferred to an atmosphere of 100 percent relative humidity at 99°F. Thirty minutes later, the specimens are immersed in distilled water at room temperature.

The ends of the cylinder shall be surfaced at right angles to the axis. The ends of the specimens may be ground flat by the use of a small amount of carborundum powder (200 mesh) and water. The molds containing the specimens are drawn back and forth across a glass plate coated with the abrasive and water. They should be rotated about one-fourth turn every few strokes. The test specimens shall be kept wet during the grinding and until after crushing. The machine used in crushing the test specimens shall be operated at a rate of speed which will move the crushing head 0.25 per minute.

The value for compressive strength shall be reported as the average of three or more from a lot of five specimens and shall be rounded off to the nearest 10 kg. per square centimeter (150 pounds per square inch). If the values for individual specimens vary more than 15 percent from the average, they shall be discarded and the average of the remaining specimens shall be reported. In case more than two of the specimens are eliminated, the test shall be repeated.

I. Film Thickness: A portion of a mix of standard consistency is placed between two flat square or round plates of uniform thickness. The surfaces of the plates between which the cement is spread shall be approximately 2 square centimeters. Three minutes after the mix is started, a load of 15 kg. shall be applied vertically on the top plate.

Ten minutes after the mix is started, the thickness of the two plates with the cement film between them shall be determined. The difference in the thickness of the plates with and without the cement film shall be considered as the film thickness. An average of three tests shall be reported to the nearest 5 microns (0.0002 inch).

J. Disintegration. The disintegration of a cement is a measure of the erosion plus the extraction of soluble material from the cement by the action of water.

One-half cubic centimeter (0.5 cc) of cement of standard consistency is pressed between two flat plates until the cement is 20 mm in diameter. (A piece of waxed thread placed in the soft cement before the specimens are formed provides a convenient means of holding the specimens). Three minutes after the mix is started, the plates and cement are placed in an oven at 99°F for one hour. Two such specimens shall be used for each determination.

After one hour, the specimens are withdrawn from the oven and quickly weighed. The combined weight of the two, less the weight of the waxed threads, shall be

taken as the weight of the specimens of cement. The specimens are immediately submerged in 100 cc of distilled water in a weighed stoppered flask and stored for a period of seven days at 99°F. The specimens are then removed from the water. There shall be no evidence of crystal growth or extensions from the surface of the specimen. The water is evaporated at a temperature just below 212° F. The flask is then dried at 300°F to constant weight. The flask and contents are weighed. The difference between the final weight of the flask and its initial weight is the amount of disintegration. The gain in weight divided by the weight of the specimens times 100 gives the percentage of disintegration. The average of duplicate tests (two flasks containing two specimens each) shall be reported to the nearest 9.1 percent.

K. Packaging: K-1. The cement powder and liquid shall be supplied in glass containers. The net weight of the powder shall be indicated on the container. The liquid shall be supplied in an amount 20 percent in excess of that necessary to combine with the total amount of powder when mixed to testing consistency.

K-2. Adequate and accurate instructions for proportioning and manipulation shall accompany each package. These instructions shall include the temperature of the slab, the powder:liquid ratio, the rate of powder incorporation and the time of mixing.

K-3. Each package of powder and liquid shall be marked with a serial number or a combination of letters and numbers which shall refer to the manufacturer's records for that particular lot or batch of cement powder and liquid.

K-4. The date of manufacture (year and month) shall be indicated on the package as a separate item or as a part of the serial number.

L. Notes: L-1. Manufacturers of dental cements may indicate that their materials comply with this specification by: (a) a statement on the package guaranteeing the material contained therein to meet the requirements of this specification; or (b) a statement of the physical properties of the material in such detail as to cover all of the requirements specified. "

Methods for Testing the Properties of Cement Materials.

-o-

A. For the Powder:

1. Chemical Composition:

The desired composition of the powder was made by combining chemicals of reagent grade in the required proportions.

2. Specific Gravity:

This determination was made with a procedure developed by the Bureau of Standards for use where the testing of a very fine powder was involved. The procedure follows:

"1.- Weight of Sample.

A clean, stoppered pycnometer is weighed and approximately ten grams of powdered sample (measured) is put into pycnometer through a small glass funnel. Pycnometer is brushed to remove particles clinging to outside, stoppered and weighed.

2.- Vacuum Treatment.

After weighing, stopper is left in balance case; pycnometer is transferred to bell-jar which is then sealed at bottom with a specially prepared stop-cock grease and at the top with a rubber stopper through which passes a block tin tube suitably bent for supplying water to all pycnometers by rotation.

Bell-jar is then connected to vacuum line and pump is started, and the pressure is reduced 710 mm before any water is added to the pycnometer.

The distilled water used should not be over 20°C and should be added in small amounts, beginning with just enough to cover sample completely.

Sample and water must be stirred or shaken thoroughly (best accomplished by imparting a rotating motion to the entire bell-jar) each time water is added.

When the pycnometer is approximately two-thirds full, no more water is added until the majority of fine particles, which have been floating, sink to bottom by the shaking action mentioned above.

The pycnometer is then filled to top of neck and allowed to stand under reduced pressure indicated previously until free of air.

The vacuum line at the bell-jar is closed and the entire apparatus disconnected from the vacuum line. The atmosphere is then slowly admitted to the bell-jar.

Pycnometer is removed, wiped dry, placed in balance case, filled with water from medicine dropper, stoppered, wiped dry again and weighed. This gives the weight of the pycnometer, the water and sample.

Immediately after weighing, remove stopper and insert thermometer, press down gently until thermometer bulb rests on the bottom of pycnometer and record the temperature.

3. Calculation.

M = Specific gravity, where M = mass or weight, and v = volume of sample or volume of water displaced by sample.

Simplified blank forms have been provided for recording of weights and temperatures. Each form accommodates one set of four pycnometers and is so designed as to reduce manipulations of figures during calculation to a minimum.

A table of water densities, ranging from 20 to 35 degrees C., with divisions at every tenth part of a degree, has also been provided. These densities were taken from Table 37, Bureau of Standards Circular No. 19, Page 53.

The following data has been obtained:

A. Weight of pycnometer
B. Weight of pycnometer - sample
C. Weight of sample of difference
D. Weight of pycnometer - sample - water
E. Temperature of sample and water
F. Volume of pycnometer previously calibrated by comparison (see table)

Then:

$$S.G. = \frac{\text{Weight of Sample}}{\text{Vol. of Pyc.} - \left(\frac{\text{Wt. pyc. + Sample + H O)-(Wt.pyc. + sample)}}{\text{Density of water at recorded temp.}} \right)}$$

4. Calibration of Pycnometers:

Pycnometers used in this work should be calibrated to determine their volume and should be recalibrated as often as is necessary to insure accurate and uniform results. This is done by determining the weight of water which they contain at a given temperature and dividing by the density of water indicated in the table for that temperature.

5. Tolerance.

On check determinations of specific gravity of solids, the difference in two determinations should not exceed 0.005 (sp.gr.) and in calibrations of pycnometers 0.0008 (vol.)

3.- Particle Size and Size Distribution.

A powder sample was examined through a microscope equipped with a calibrated ocular micrometer. The following characteristics were noted:

1. Size of Largest Particles
2. Size of Smallest Particles
3. Size, Range of any Maximum Number of Particles (if a size-region exists that contains an obvious excess of particles).
4. Shape of Particles

B.- For the Liquid:

1. Chemical Composition.

The liquid was made by using chemicals of known composition and combining them to produce the desired product.

2. Specific Gravity:

This property was determined by means of a pycnometer.

3. For the Mixed Cement:

The mixed cement that was tested was prepared in the following manner:

The mixing was done on a thick glass slab approximately three by six inches, that had been cooled to a temperature somewhere between 65 F and 75 F. One gram of the powder was placed on the slab, divided into approximate quarters. One of these quarters was further

subdivided into an eighth and two sixteenths. The liquid was measured out on the slab by means of a hypodermic syringe, one-half a cubic centimeter being used. (See Fig. 6). The powder and the liquid were not allowed to come into contact with one another until the mixing started. A stiff dentist's spatula was used in mixing. A stop watch was started. At the same time, the first sixteenth of the powder was drawn into the liquid and spatulated thoroughly. At the end of ten seconds, the second sixteenth was drawn in and spatulated for ten seconds. Then the one-eighth portion was treated in like manner. Thus, thirty seconds were consumed. The next two quarter portions were added separately and spatulated in fifteen second intervals, and the final quarter was then added and spatulated for thirty seconds.

Nearly one-half of the slab was used in making the mix. No crumbs of powder or unused liquid were allowed to collect at the edge of the mix, every portion of powder being thoroughly incorporated. A rotary motion of the spatula, with light pressure in combination with a scraping motion which would pick up the cement and deposit in a heap, was alternately used.

The cement was spread over the slab in mixing to prevent the heat of reaction from raising the temperature of the mix.

All tests on the mixed cement were made with mixes prepared in the above manner.

1. Setting Time. (Bureau of Standards Method (5).

> "A ring three-eighths inch in diameter and three-sixteenths inch high was filled with the soft cement (see Fig. 4). A Gilmore needle weighing 1 pound and having a point one-twenty-fourth inch in diameter was used to determine the setting time. The needle was lowered vertically until the surface of the cement was touched. The contact was made for five seconds under the full weight of the needle. When no indentation on the cement surface was discernible, the cement was considered set. The setting time was therefore the interval between the commencement of the mix and the completion of the set. The time of set is reported to the nearest minute. For this test, it is absolutely essential that all of the apparatus be clean; especially, that they shall be free of all particles of set cement."

The setting time was determined under two conditions, room and oral. For room conditions, the cement was allowed to set on a glass plate in a temperature between 20 and 25 C and the normal humidity encountered. For oral conditions, it was allowed to set in an atmosphere of 99 F and saturation (see Fig. 4).

2. Consistency of Unset Cement.

(Bureau of Standards Method (4)).

"The apparatus used to measure consistency is shown in Figure 7. It consists of: (1) a glass tube B graduated on one end to indicate 0.5 cc; (2) a heavy rubber plug C inside the tube at the calibration mark; (3) a thin cellophane disk D adjacent to the rubber plug (this preventing adherence of the sticky cement to the rubber plug); (4) a glass plunger A which forces the rubber plug, cellophane disk and soft cement from the tube; (5) two glass plates H and a 100 gm weight G which press the cement between them into the disk 1. The method of determining the consistency is as follows: Trial amounts of powder are mixed with 0.5 cc of liquid. One-half cubic centimeter of the soft cement is deposited on a slab. A flat glass plate (20 gm) and a weight (100 gm) are placed (parallel to the bottom plate) upon the cement three minutes after the mixing was started. The soft cement spreads out into a disk between the glass plates. Ten minutes after the mixing was started, the diameters of the disk are measured."

3. Film Thickness of Cement.

(Bureau of Standards Method (4)).

"A portion of a mix of cement was placed between two pieces of clean glass 2 cm long and 1 cm wide. The pieces of glass were flat and of uniform thickness. The mix was completed in one and a half minutes and the same time was consumed in placing the cement on the glass surfaces. Three minutes after the mix was started, the load (14 kg) was applied vertically on the top plate. Seven minutes later, the thickness of the plates

with the cement film between them was measured with a thickness gage. The difference between this measurement and the original thickness of the glass plates was taken as the film thickness."

-o-

BIBLIOGRAPHY

-o-

(1) Fleck, Herman "Chemistry of Oxyphosphates" Dental Items of Interest, 24 Dec. 1902

(2) Poetschke, P. "Physical Properties of Dental Cements" Journal of Industrial and Engineering Chemistry, 8 April 1916

(3) Marcus L. Ward & Ralph M. McCormick "The First Report of the Study of the Cements Now in Use In Dentistry" Journal of the American Dental Association" November 1915

(4) George C. Paffenbarger, W.T.Sweeney, and Aaron Isaacs "Zinc Phosphate Cements: Physical Properties and A Specification" Journal of The American Dental Association Nov. 1934

(5) George C. Paffenbarger, W. T. Sweeney, and Aaron Isaacs "A Preliminary Report on the Zinc Phosphate Cements" Journal of the American Dental Association Nov. 1933

-o-

This research was made possible by a grant of $250.00 from the Whip-Mix company, of Louisville, Kentucky. The author gratefully acknowledges their interest and the aid of Mr. Robert Neiman, of that company, in the investigative work.

-o-